

# Electrochemical remediation of BPA in a soil matrix by Pd/Ti and RuO<sub>2</sub>/Ti electrodes

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Received: 31 May 2013 / Accepted: 3 August 2013 / Published online: 15 August 2013  
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**Abstract** This study aimed to investigate the bisphenol A (BPA) degradation performance of an electrokinetic process coupled with Pd/Ti (PT) and RuO<sub>2</sub>/Ti (RT) binary metallic oxidation electrodes under a potential gradient of 2 Vcm<sup>-1</sup> for 5 days. Fifteen experiments conducted with five processing fluids, namely deionized water (DW), Na<sub>2</sub>SO<sub>4</sub>, citric acid (CA), NaOH and NaCl, and two binary metallic oxidation electrodes, Pd/Ti and RT, were investigated in this study. Electroosmosis permeability of  $3.2 \times 10^{-6}$ – $4.7 \times 10^{-6}$ ,  $4.0 \times 10^{-6}$ – $4.9 \times 10^{-6}$ , and  $3.7 \times 10^{-6}$ – $6.8 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were observed in the electrokinetic system with Ti, PT, and RT electrodes, respectively. A significant detachment of the coated metals was observed in BMOEEK–PT system with Na<sub>2</sub>SO<sub>4</sub>, CA, and NaOH processing fluids. A higher BPA treatment efficiency of 52.2–67.3 % was found in the BMOEEK–RT system, which was 1.4–1.8 times greater than in the EK–Ti system with DW as the processing fluid. The best treatment efficiency was found in the system with NaCl as the processing fluid, which may mostly result from less detachment of the coated metal from electrode and increased hypochlorite (OCl<sup>-</sup>) generation in the anode reservoir. The

primary treatment mechanism in the BMOEEK system with NaCl procession fluid was degradation by anodic oxidation. It was concluded that both the binary metallic electrode and processing fluid played key roles in enhancing the electrochemical degradation of BPA. The electrode characteristics (progressive cyclic voltammogram and SEM micrograph with EDAX), electrokinetic behavior (specimen pH and current density), and treatment mechanism were also discussed in this study.

**Keywords** Binary metallic oxide electrode · Bisphenol A · Electrokinetic process · Soil remediation

## 1 Introduction

Bisphenol A (BPA) is an environmental hormone that is widely distributed in the environment. The wide use of plastic products has resulted in the serious environmental pollution of BPA. In the USA, 230 billion pounds of BPA was applied in epoxy and electronic products [1]. As the environmental pH and temperature change, the BPA inside the above-mentioned products is released into environment, increasing the exposure potential for humans. Vandenberg et al. [1] reported that the concentration of BPA in air and particulate matter is 208 ng m<sup>-3</sup> and 17 µg g<sup>-1</sup>, respectively. Previous studies reported that the exposure concentration of BPA for adults has reached 1.47 µg kg<sup>-1</sup> days<sup>-1</sup> in Europe, resulting in 0.3–18.9 ng mL<sup>-1</sup> of BPA in blood [2, 3], 0.2–9.2 ng mL<sup>-1</sup> in umbilical cord blood, and 104.9 ng g<sup>-1</sup> in human placenta [3]. As the concentration of BPA in the human body increases, the endocrine system will eventually be destroyed and breast cancer may develop [4]. The common treatment technologies for BPA have focused

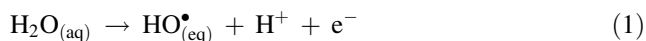
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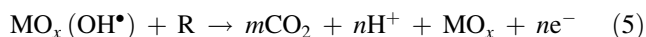
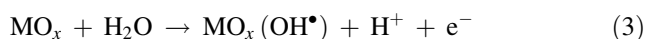
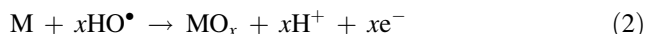
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on aqueous media, such as photocatalysis [5] and chemical oxidation [6, 7]. Few reports have addressed remediation in sediment [8] and in soil.

Chemical oxidation technology has been demonstrated to provide good degradation performance for environmental hormone, phenol, and chlorinated organics in the aqueous phase [9]. The advantages of this technology include its easy operation, high mineralization efficiency, and low cost. This technology forces some non-spontaneous electrochemical reactions to occur via electron transfer between the electrolyte solution and reaction electrodes. Two pathways result in the degradation of organic compounds in chemical oxidation process: One is directly reacted with high-reactivity electrodes, and the other is reacted with OH radicals produced in the anode reservoir [10]. In aqueous electrochemical reactions, OH radicals would be produced from the hydrolysis of water as shown in Eq. (1):



The degradation of organics by metallic electrodes was reported by Awad and Galwa [13]. The OH radical reacts with metals coated on the electrode surface by Eq. (2) to form metallic oxides ( $\text{MO}_x$ ). The  $\text{MO}_x$  then reacts with water to form  $\text{MO}_x(\text{OH}^\bullet)$  by Eq. (3). The organic compounds (R) degrade to  $\text{CO}_2$  by  $\text{MO}_x$  and  $\text{MO}_x(\text{OH}^\bullet)$ , as shown in Eqs. (4) and (5).



where M is the metal coated on the electrode surface, and  $m$  and  $n$  are the stoichiometric coefficients of the  $\text{CO}_2$  produced and electrons transferred, respectively.

The electrodes applied in electrochemistry are classified into three types: inert electrodes, metal electrodes, and composite electrodes. The last two above-mentioned electrodes are the most common use electrodes because of higher reactivity and larger free electrons production [11, 12]. Binary metallic oxidation electrodes, such as  $\text{PbO}_2$ -Co/Ti,  $\text{RuO}_2$ /Ti (RT), Pd/Ti (PT), and  $\text{SnO}_2$ /Ti, are a kind of metal electrodes, which have been applied in chemical oxidation processes [11, 13, 14]. Recently, the binary metallic oxidation electrodes showed a good degradation performance for environmental hormones [7, 9, 15–17]. Tanaka et al. [7] applied a Pt/Ti electrode to BPA degradation, revealing that the degradation efficiency was 80 % in  $\text{Na}_2\text{SO}_4$  solution with an applied voltage of 0.75–1.05 V for 30–50 min. Kim et al. [9] applied a  $\text{PbO}_2$ -Co/Ti electrode in 0.1 M  $\text{Na}_2\text{SO}_4$  solution to degrade nonylphenol

(NP), TX-100, and phenol. It was found that the degradation of NP reached 100 % with a current density greater than  $25 \text{ mA cm}^{-2}$ , which was resulted from a higher production of OH radicals in the system. Kuramitz et al. [15] reported that BPA (0.1 mM) was almost completely degraded within 60 min by an electrochemical technique with a carbon fiber electrode and an applied voltage of 1.0 V. Yuan et al. [16, 17] applied a series of binary metallic oxidation electrodes to investigate regeneration performance of carbon nanotubes adsorbed with  $150 \text{ mg L}^{-1}$  NP by electrokinetic process. A regeneration efficiency of 50.6–64.2 % was found in EK system with  $\text{PbO}_2$ /Ti electrode applied 2 V/cm for 5 days [16] although coating of Co and insulated layer of  $\text{SnO}_2 + \text{Sb}_2\text{O}_3$  onto the PT electrodes resulted in a higher regeneration efficiency to 52.0–80.0 %. However,  $1.0 \times 10^{-3}$ – $1.7 \times 10^{-2} \text{ mg}$  of  $\text{Pb}^{2+}$  detachment was found within 72 h, which results in water pollution [16]. Hence,  $\text{MnO}_2$ /Ti (MT) and RT electrodes were developed and investigated [17]. Results indicated that RT electrode with NaCl electrolyte solution showed a highest regeneration efficiency of 77.0 %. A precious metal of palladium (Pd) coated on Ni foam was successfully applied in electrochemical reductive dechlorination of organic solvents [18–20]. Yang et al. [18] reported that a degradation efficiency of 94.6 % for 4-chlorobiphenyl was reached within 2 h by Pd/Ni foam electrode with 50 % methanol. Wang et al. [19] also reported that 96.2 % tetrachlorophenol was degraded within 2 h by Pd/Ni foam electrode at solution pH of 4. However, less degradation efficiency (70 %) of 2,4-dichlorophenoxyacetic acid was found by Pd/Ni foam electrode [20]. The palladium may become a potential metal for reactive electrode preparation.

Electrokinetic (EK) remediation is a promising in situ technique for decontamination in low hydraulic permeability media. Basically, the EK technique relies on the action of an electric field generated between inserted electrodes in the medium by applying a direct current or a constant voltage. The applied potential causes the migration of electrolyte solution and soluble contaminants toward the electrodes via electromigration, electroosmosis, and electrophoresis [21]. Various enhancement techniques, e.g., careful control of the pH within the electrode [22], use of chelating agent [23], and use of enhancing reagents [24] in the cathode reservoir have been proposed to improve effectiveness of EK system. The key feature for improving EK performance was highly dependent on the interaction between the contaminants and processing fluid. Additional parameters affecting the EK performance were included, namely, potential gradient and processing time, which were highly dependent on the characteristics of the soils and contaminants. However, EK only can remove and concentrate contaminants to the counter electrode reservoir.

Hence, there is a strong need for an upgraded vision of the EK process to create a sustainable technology for both the removal and the degradation of pollutants.

In EK process, substituting inert electrodes with binary metallic oxidation electrodes will decompose pollutants. After evaluating potential binary metallic oxidation electrodes, this study aimed to investigate the degradation of BPA in a soil matrix by  $\text{RuO}_2/\text{Ti}$  and  $\text{Pd}/\text{Ti}$  electrodes in a BMOEEK (binary metallic oxidation electrode-electrokinetic process) system under a potential gradient of  $2 \text{ V cm}^{-1}$  for 5 days. The characteristics of the binary metallic oxidation electrodes and the BPA treatment mechanism will be discussed.

## 2 Experimental materials and methodology

### 2.1 Characteristics of BPA

Reagent-grade BPA was purchased as from Aldrich, USA. The chemical formula of BPA is  $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$ , which is very similar to that of  $17\beta$  estradiol, a natural hormone. BPA is denser than water, exhibiting a specific gravity of 1.2 and is difficult to diffuse into air, having a vapor pressure of 5.2 mmHg at  $20^\circ\text{C}$  [25]. BPA easily dissolves in most organic solvents but is less soluble in aqueous solution with aqueous solubility of  $120 \text{ mg L}^{-1}$  [25]. BPA has a high affinity in the soil phase with a  $\log K_{\text{ow}}$  of 3.2 (at  $20^\circ\text{C}$ ) [25], resulting in low mobility in the subsurface environment. The  $\text{pK}_a$  of BPA is 9.6 [25].

### 2.2 Soil and processing fluid

Soil samples were collected from a depth of  $\sim 0.7$ – $1.5 \text{ m}$  below the surface within a farmland located in southern Taiwan. The texture of the soil sample was classified as clay by particle-size analysis. A soil organic matter content of 3.73 % was observed by the combustion method [26]. A soil pH of 8.5 was measured in water suspensions with a 1:1 volume ratio of soil to solution, and a soil  $\text{pH}_{\text{ZPC}}$  of 2.4 was determined by a zeta potential instrument (Pen Kem-Laser Zee 3.0, USA). A soil solid density of  $2.12 \text{ g cm}^{-3}$  was determined according to the method of ASTM D854-92. A soil-specific surface area of  $14.8 \text{ m}^2 \text{ g}^{-1}$  was measured by a BET surface area analyzer (ASAP 2010, Micromeritics, USA). The hydraulic conductivity of the soil sample was less than  $10^{-8} \text{ cm s}^{-1}$  as measured by a falling-head permeameter.

After debris removal and air-drying, the soil sample was passed through a sieve of less than 2 mm and then treated by pressure sterilization at 118 kPa for 5 min. The BPA-contaminated soil was prepared by adding 27 mg of BPA, 100 mL of methanol, and 900 g of sieved soil into a 2-L

glass beaker. To obtain a uniformly BPA-spiked soil sample, the soil mixture was stirred to vaporize the methanol completely. To measure the BPA concentration, 5 g of spiked soil was extracted with 15 mL of methanol at 150 rpm for 20 min and the concentration of BPA in the extract was determined by HPLC–UV (Hitachi, L-2000 series, Japan) coupled with an  $\text{NH}_2$  Hypersil APS-2 $\text{NH}_2$  ( $250 \times 4.6 \text{ mm}$ ,  $5 \mu\text{m}$ ) column and detected at a wavelength of 275 nm. Triplicate soil samples were analyzed for quantification. The BPA-spiked soil was then ready for the subsequent EK experiments.

The solubility of BPA was considered to be key feature to select processing fluid. The BPA was more soluble at high pH, and the effect of the oxidation agent on BPA degradation was needed to investigate. Therefore, NaCl (0.1 M) and  $\text{Na}_2\text{SO}_4$  (0.1 M) were selected as the processing fluids for testing. The control tests used citric acid (CA) (0.1 M) and deionized water (DW) as processing fluids for comparison. All processing fluids were of reagent grade and purchased from SHOWA, Japan.

### 2.3 Preparation of binary metallic oxide electrodes

The preparation of the  $\text{Pd}/\text{Ti}$  electrode was carried out according to the method described by Sun et al. [27]. The Ti electrode was etched in 200 mL of 0.5 M  $\text{H}_2\text{SO}_4$  solution for 1 h. The etched Ti electrode was then washed with 1 L of DW and soaked in 100 mL of 22.6 mM  $\text{PdCl}_2$  solution before being used as the working electrode. An electric current of  $12.5 \text{ mA cm}^{-2}$  was applied to the  $\text{PdCl}_2$  solution for 17 min. Finally, the PT was washed with 1 L of DW and air-dried for use in the experiments.

The preparation of the RT electrode was carried out accordingly to method described by Yang et al. [11]. The Ti electrode was etched in 6 M HCl solution for 1 h at  $80$ – $90^\circ\text{C}$  and a mixed solution of 10 mL of iso-propyl alcohol and 90 mL of HCl solution was prepared. After drying for 30 min at room temperature, the etched Ti electrode was soaked in the above-described mixed solution with 0.5 g of  $\text{RuCl}_3$  for 1 min and then placed in a vacuum oven ( $85$ – $90^\circ\text{C}$ ) for 10 min of drying. Next, the etched Ti electrode was calcited at  $450^\circ\text{C}$  for 10 min. The soaking and calcitation procedures were repeated five times. Finally, the electrode was calcited again at  $450^\circ\text{C}$  for 1 h, after which it was ready for use in the experiments.

### 2.4 Cyclic voltammetry (CV) measurement

Voltammetric measurements were carried out with a voltammetric analyzer (Autolab PGSTAT 302). The binary metallic oxidation electrode of interest was used as the working electrode. Prior to the experiments, the electrode was cleaned with DW. A platinum wire was used as a counter

electrode, and all potentials were recorded against an Ag/AgCl reference electrode. The cyclic voltammograms were measured in 3.0 M potassium chloride solution within range of  $-0.5$  to  $2.0$  V at a rate of  $0.05$  V s $^{-1}$  six times.

## 2.5 Electrokinetic experiments

Fifteen experiments were conducted in an acrylic cell of  $4.2$  cm ( $\phi$ )  $\times$   $22$  cm (L). The cell consisted of three compartments, as shown in Fig. 1: the cathode reservoir (5 cm in length), anode reservoir (5 cm in length), and soil specimen chamber (12 cm in length). The processing fluid was initially added into both the anode and cathode reservoirs and replenished in the anode reservoir every 12 h. The stainless steel electrodes and investigated binary metallic electrodes were inserted into the anode and cathode reservoir, respectively. All experiments were conducted under a potential gradient of  $2.0$  V cm $^{-1}$  for 5 days. During the experimental periods, the effluent from the anode and cathode reservoirs, which was defined as electroosmotic flow ( $Q_e$ ), was collected and measured. The electric current and concentration of BPA in the reservoir were monitored during the experimental periods. The current density was calculated by dividing the electric current by the cross-sectional area of the cell. Eight soil pHs were determined after each test, which was determined according to the ROC-EPA method. Among these pHs, one each was sampled at the end of anode and cathode side, and the other six were sampled every 2 cm of soil specimen. The BPA concentration was determined by HPLC–UV (Hitachi, L-2000 series, Japan) coupled with a NH $_2$  Hypersil APS-2NH $_2$  column ( $250 \times 4.6$  mm,  $5$   $\mu$ m) and detected at a wavelength of  $275$  nm.

## 2.6 Detaching test of electrodes

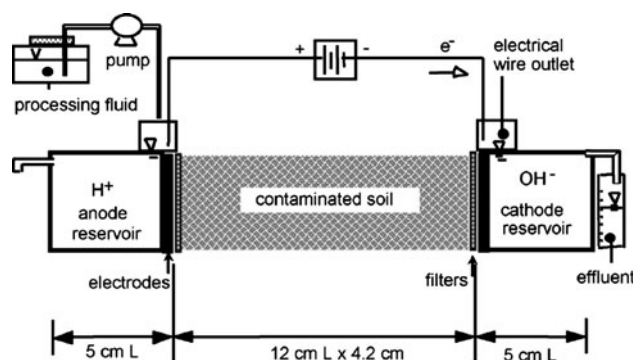
The investigated PT and RT electrodes were soaked in five processing fluids, and the direct current was connected to the electrodes with potential gradient of  $2$  V cm $^{-1}$ . The concentration of Pd $^{2+}$  and Ru $^{2+}$  in the electrolyte solution was analyzed every 5 days by ICP (Optima 2000DV, Perkin Elmer).

## 3 Results and discussion

A summary of the results of the electrochemical remediation of BPA in the three investigated systems is shown in Table 1 and is further discussed in the following sections.

### 3.1 Performance of binary metallic oxide electrodes

According to preparation method described in Sect. 2.3, the amount of metal on electrodes was quantified with ICP



**Fig. 1** Setup of binary metallic oxidation electrode-electrokinetic system (BMOEEK)

followed by microwave digestion. The results showed that  $1.60 \pm 0.09$  % (by wt) of Pd $^{2+}$  and  $1.42 \pm 0.15$  % (by wt) of Ru $^{2+}$  were coated on the respective electrodes.

The current in the cyclic voltammogram represents the electrode reaction rate. In general, the current is governed by the rates of the following processes: (1) mass transfer; (2) electron transfer at the electrode surface; (3) chemical reactions preceding or following electron transfer, such as protonation or dimerization reactions; and (4) other surface reactions, such as adsorption or electrode deposition [28]. When the applied voltage in the investigated systems exceeded the corresponding voltage of the peak current in the cyclic voltammograms, the anode oxidation would be triggered in the BMOEEK system.

Due to its low reactivity, no response for the Ti electrode was shown in the cyclic voltammograms. Figures 2 and 3 showed progressive cyclic voltammograms of PT electrode in 0.1 M CA, 0.1 M Na $_2$ SO $_4$ , 0.1 M NaOH, and 0.1 M NaCl with and without  $2.5$  mg L $^{-1}$  BPA, respectively. Figures 4 and 5 showed progressive cyclic voltammograms of RT electrode in 0.1 M CA, 0.1 M Na $_2$ SO $_4$ , 0.1 M NaOH, and 0.1 M NaCl with and without  $2.5$  mg L $^{-1}$  BPA, respectively. The results showed that the electrode response of these solutions is a typical irreversible electrode reaction. The corresponding voltages of the peak currents in PT systems in processing fluids of CA, Na $_2$ SO $_4$ , NaOH, and NaCl with  $2.5$  mg L $^{-1}$  BPA occurred at  $-0.2$ ,  $-0.59$ ,  $-0.6$ , and  $-0.61$  V, respectively (Fig. 2), which were lower than those in the procession fluid solutions without BPA (Fig. 3). Similarly, the corresponding voltages of the peak currents in the RT system with the above four solutions occurred at  $0.65$ ,  $1.2$ ,  $1.2$ , and  $0.2$  V (Fig. 4), respectively, which were also lower than those in the procession fluid solutions without BPA (Fig. 5). The results showed that it was easier to initiate the oxidation of both PT and RT in NaCl solution. For these two electrodes, the corresponding potentials of the peak current in the PT system with the above four solutions was lower than in RT

**Table 1** Summary results of electrochemical remediation of BPA in BMOEEK systems

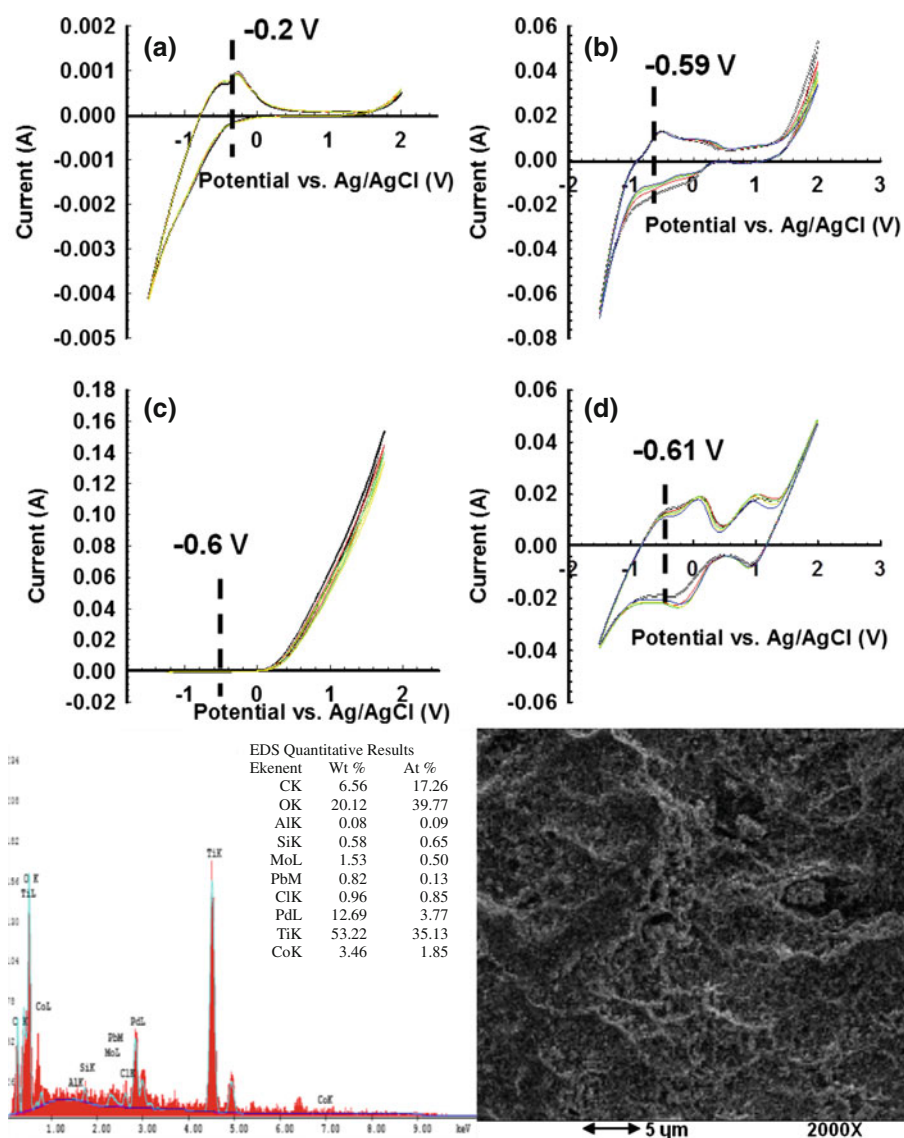
Test no.	(1) Experimental system	(2) Processing fluid	(3) $Q_e$ (cm <sup>3</sup> day <sup>-1</sup> )	(4) $k_e$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	(5) Power consumption (kWhm <sup>-3</sup> )	Fractions of BPA				(10) Removal efficiency (R) (%)	(11) Degradation efficiency (η) (%)	(12) Treatment efficiency <sup>c</sup> (Y) (%)	
						(6) Solid phase (S) (%)	Reservoir (%)		(7) Collected				(8) Degraded
							Anode	Cathode collected					
1	EK-Ti	DI water	10.6	$4.4 \times 10^{-6}$	748.5	62.0	7.8	15.0	15.2	23.0	15.0	38.0 (1.0) <sup>d</sup>	
2		Na <sub>2</sub> SO <sub>4</sub> (0.1 M)	7.6	$3.2 \times 10^{-6}$	541.2	59.0	13.2	13.7	14.1	27.3	13.7	41.0 (1.1) <sup>d</sup>	
3		Citric acid (0.1 M)	7.5	$3.6 \times 10^{-6}$	597.5	50.2	15.4	18.9	15.5	31.0	18.9	49.8 (1.3) <sup>d</sup>	
4		NaOH (0.1 M)	11.3	$4.7 \times 10^{-6}$	748.5	53.5	12.6	19.9	14.0	26.6	19.9	46.5 (1.2) <sup>d</sup>	
5		NaCl (0.1 M)	9.5	$4.2 \times 10^{-6}$	603.2	48.8	10.4	30.2	10.6	21.0	30.2	51.2 (1.3) <sup>d</sup>	
6	BMOEEK-PT <sup>a</sup>	DI water	11.7	$4.9 \times 10^{-6}$	643.1	48.3	10.7	31.0	10.0	20.7	31.0	51.7 (1.4) <sup>d</sup>	
7		Na <sub>2</sub> SO <sub>4</sub> (0.1 M)	11.1	$4.6 \times 10^{-6}$	508.2	47.6	10.8	32.3	9.2	20.1	32.3	52.4 (1.4) <sup>d</sup>	
8		Citric acid (0.1 M)	9.5	$4.0 \times 10^{-6}$	548.1	42.2	6.4	35.3	16.0	22.4	35.3	57.8 (1.5) <sup>d</sup>	
9		NaOH (0.1 M)	10.1	$4.2 \times 10^{-6}$	643.1	43.4	4.5	36.4	15.7	20.2	36.4	56.6 (1.5) <sup>d</sup>	
10		NaCl (0.1 M)	11.1	$4.6 \times 10^{-6}$	597.2	35.6	ND	51.5	12.9	12.9	51.5	64.4 (1.6) <sup>d</sup>	
11		BMOEEK-RT <sup>b</sup>	DI water	16.2	$6.8 \times 10^{-6}$	721.5	47.8	9.9	27.8	14.5	24.4	27.8	52.2 (1.4) <sup>d</sup>
12	Na <sub>2</sub> SO <sub>4</sub> (0.1 M)		10.6	$4.4 \times 10^{-6}$	598.2	44.7	6.9	36.5	12.0	18.8	36.5	55.3 (1.5) <sup>d</sup>	
13		Citric acid (0.1 M)	9.3	$3.9 \times 10^{-6}$	592.4	39.6	8.0	40.4	12.0	20.0	40.4	60.4 (1.6) <sup>d</sup>	
14		NaOH (0.1 M)	8.8	$3.7 \times 10^{-6}$	542.4	39.8	8.9	41.2	10.1	19.0	41.2	60.2 (1.6) <sup>d</sup>	
15		NaCl (0.1 M)	9.0	$3.8 \times 10^{-6}$	648.5	32.7	ND	61.0	6.3	6.3	61.0	67.3 (1.8) <sup>d</sup>	

(6), fraction of BPA retained in soil; (10), fraction of NP removed to reservoirs; (11), fraction of NP degraded by electrochemical reaction; (10) = (7) + (9); (11) = (8); (12) = (10) + (11)

<sup>a</sup> Pd/Ti electrode<sup>b</sup> RuO<sub>2</sub>/Ti electrode<sup>c</sup> Fractions of removed and degraded NP<sup>d</sup> Compared to treatment efficiency of Test 1



**Fig. 2** Progressive cyclic voltammogram for PdO<sub>2</sub>/Ti electrode in solution of **a** 0.1 M citric acid; **b** 0.1 M Na<sub>2</sub>SO<sub>4</sub>; **c** 0.1 M NaOH; **d** 0.1 M NaCl, and **e** SEM micrograph with EDAX chromatograph (with 2.5 mg L<sup>-1</sup> BPA)



system, which implied that the RT electrode needed a higher voltage to initiate oxidation.

Previous reports indicate that an insulating polymer film forms to block the access of BPA to the surface of the carbon fiber electrode [15, 28]. Except the case of the PT electrode in NaOH solution, the film formation was observed in each investigated binary metallic oxidation electrode system. Compared with Yuan et al. [17], the oxidation and reduction curves in the cyclic voltammograms for the PT and RT electrodes (Figs. 2, 4) were more significant for BPA than for NP for a given processing fluids.

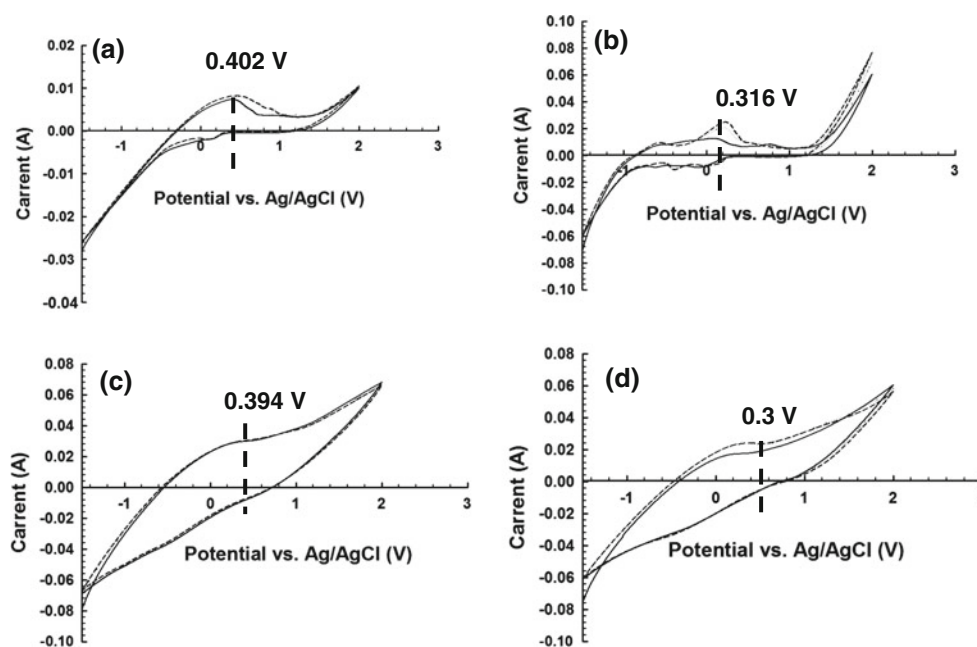
### 3.2 Electrokinetic behavior

In electrokinetic processes, the movement of an electrolyte solution driven by an electrical field, which carries the soluble pollutants toward the electrodes, is considered to be

one of the treatment mechanisms. The movement of the electrolyte solution, i.e., electroosmotic flow,  $Q_e$  (cm<sup>3</sup> s<sup>-1</sup>), for a cylindrical soil core is directly proportional to the applied electric potential gradient, i.e., (V cm<sup>-1</sup>):

$$Q_e = k_e \times i_e \times A \quad (6)$$

where  $A$  (cm<sup>2</sup>) is the cross-section area of the soil core and  $k_e$  (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) is the electroosmosis permeability. The electroosmotic flow is driven by the soil, which may be mostly due to its high surface charge density. During experimental periods, the electroosmotic flow was collected from both the anode and cathode reservoirs; hence, the average permeability was investigated throughout the EK cell. The results, shown in Table 1, indicate that higher  $Q_e$  values were found in the BMOEEK–PT systems. The  $k_e$  ranges of  $4.0 \times 10^{-6}$ – $4.9 \times 10^{-6}$  and  $3.7 \times 10^{-6}$ – $6.8 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were found in the BMOEEK–PT



**Fig. 3** Progressive cyclic voltammogram for PdO<sub>2</sub>/Ti electrode in solution of **a** 0.1 M citric acid; **b** 0.1 M Na<sub>2</sub>SO<sub>4</sub>; **c** 0.1 M NaOH; **d** 0.1 M NaCl (without BPA)

and BMOEEK–RT systems, respectively, which were higher than that in the EK–Ti system ( $3.2 \times 10^{-6}$ – $4.7 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). The magnitude of  $Q_e$  is related to the viscosity, electric field, and surface charge density on the substrate. For low potentials (Debye–Hückel approximation), the potential at the surface of the substrate scales linearly with the surface charge density on the substrate; therefore, the electroosmotic flow,  $Q_e$ , and the electroosmosis permeability,  $k_e$ , scale linearly with the surface charge density. Furthermore, for silica, the main component of soil, the surface charge is known to depend very strongly on pH [29]. Thus, the processing fluid is expected to affect the surface density of silica. It was shown that the value of  $k_e$  varied with the processing fluid in the investigated system.

The pH profiles along the experimental cell were shown in Fig. 6. In the EK–Ti system (Fig. 6a), the cell pH was as low as 3.7 near the anode side due to the H<sup>+</sup> produced from the electrolysis of water. Near the cathode side, the cell pH was as high as 11.9 because of the production of OH<sup>-</sup> from water electrolysis. Similar cell pH trends were of cell pH which was found in the other two systems. The cell pHs were in the range of 2.3–13.2 and 2.0–13.5 in the BMOEEK–PT (Fig. 6b) and BMOEEK–RT systems (Fig. 6c), respectively. The variation of the soil pH in the BMOEEK system was more pronounced than in EK–Ti system. Furthermore, the variation of the soil pH in the PT system was less pronounced in the RT system, which might be due in part to the very strong dependence of the surface charge of soil on pH [30] as well as electrode characteristics.

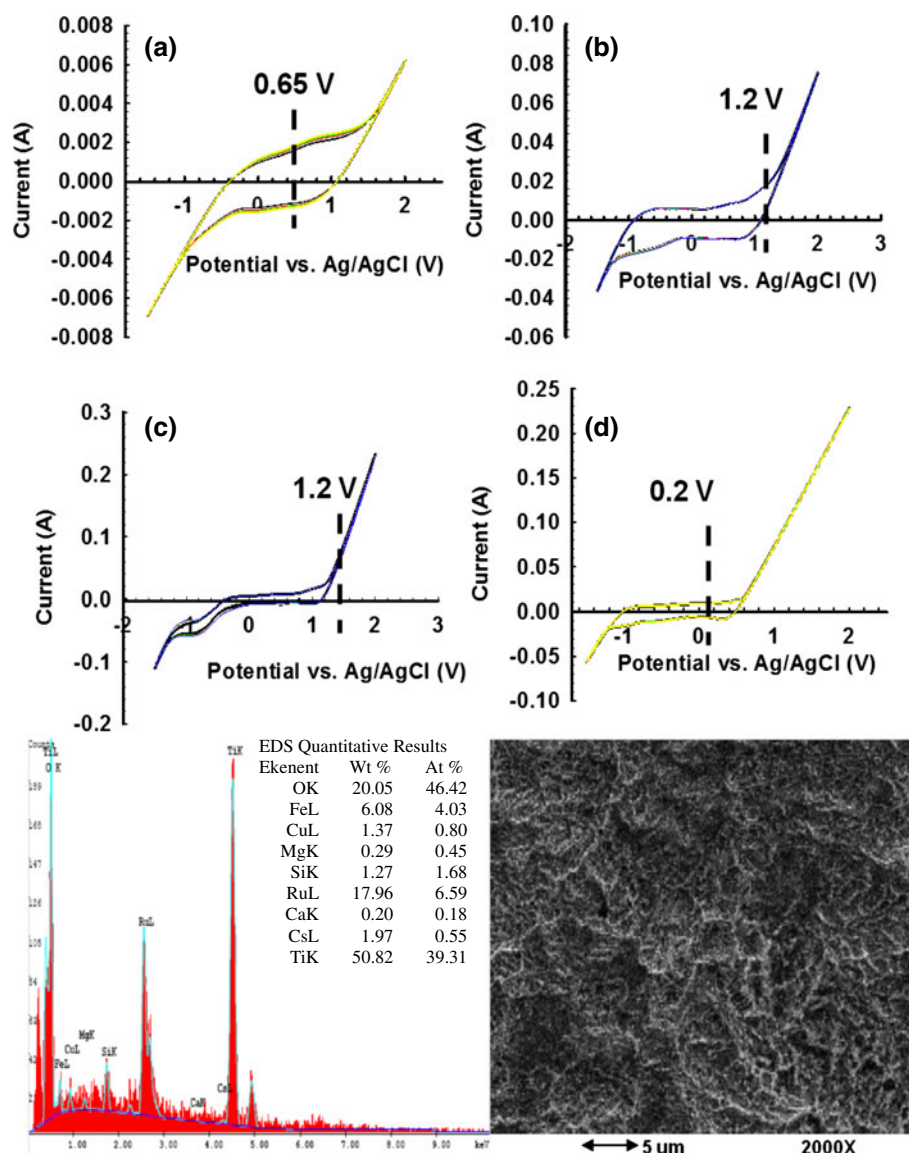
The current density results were shown in Fig. 7 for the investigated systems, which were similar to previous studies [16, 17, 30]. Conducting EK systems for more than 5 days, the current density initially increased due to electrolysis and then decreased to a low current density because of the clogging of metal precipitates [31, 32].

### 3.3 Electrochemical remediation of BPA

The electrochemical remediation of BPA was summarized in Table 1. The results indicated that the remediation performance of BPA in the investigated systems was highly related to both the electrode and processing fluid. As shown in Table 1, the treatment efficiency in Test 1, i.e., the EK–Ti system with DW, which was used as a control system, was only 38.0 %. The remediation efficiency of the BMOEEK–Ti system with Na<sub>2</sub>SO<sub>4</sub>, CA, NaOH, and NaCl processing fluids (Tests 2–5) was enhanced by a factor of 1.1–1.3. Among these fluids, the best remediation efficiency of BPA was found in the system using NaCl.

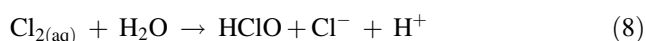
The treatment efficiency of BPA was 51.7–64.4 % (Tests 6–10) and 52.2–67.3 % (Tests 11–15) in the BMOEEK–PT and BMOEEK–RT systems, which were 1.4–1.7 times and 1.4–1.8 times greater than those in the control system (Test 1), respectively. The treatment efficiency of BPA was greatly enhanced in the BMOEEK–RT system with NaCl processing fluid, which is attributed to two factors. First, the long life cycle of the electrodes enhanced the BPA remediation performance. Figure 8

**Fig. 4** Progressive cyclic voltammogram for RT electrode in solution of **a** 0.1 M citric acid; **b** 0.1 M Na<sub>2</sub>SO<sub>4</sub>; **c** 0.1 M NaOH; **d** 0.1 M NaCl, and **e** SEM micrograph with EDAX chromatograph (with 2.5 mg L<sup>-1</sup> BPA)



showed that the coating metal detachment increased with time in all investigated systems. After 600 h, 21.7–27.0 % and 19.9–22.4 % of the metal had detached from the electrode in the BMOEEK–PT and BMOEEK–RT systems, respectively. Due to their higher oxidation and alkalinity, more coating metal was detached in the Na<sub>2</sub>SO<sub>4</sub> and NaOH solutions. Less coating metal was detached in the NaCl solution, which prolonged the life cycle of the electrode relative to that in other processing fluids.

Second, hypochlorite (OCl<sup>-</sup>), a strong oxidant, existed in the anode reservoir due to the disassociation of NaCl (as shown in Eqs. 7–9 [10]), which might contribute to BPA degradation.

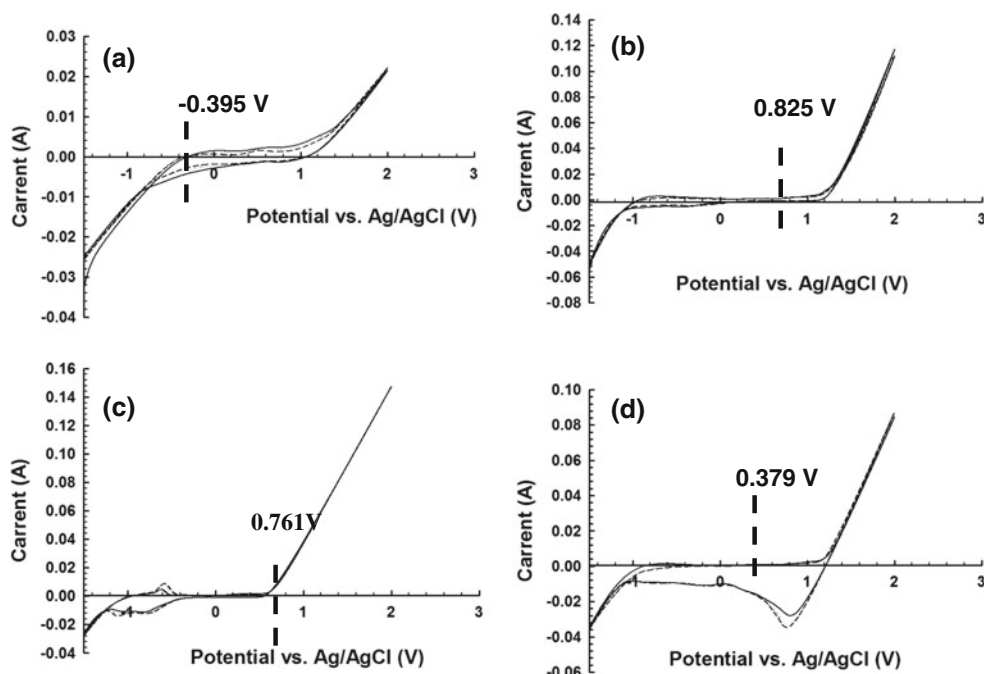


A quick test was conducted to confirm the existence of OCl<sup>-</sup> in the investigated systems. First, the investigated PT and RT electrodes were soaked in 0.1–0.4 M NaCl solutions. The electrode was connected to a direct current with a potential gradient of 2 V cm<sup>-1</sup> for 1 h, and the concentration of OCl<sup>-</sup> in electrolyte solution was analyzed by ionic chromatograph (DX-120, DIONEX, USA). The result shown in Fig. 9 indicated that OCl<sup>-</sup> existed in the systems and became more prevalent as the NaCl concentration increased. Hence, it was concluded that both OCl<sup>-</sup> and the OH radical contributed to BPA degradation in the NaCl solution, whereas the OH radical was the only contributor in the other investigated systems.

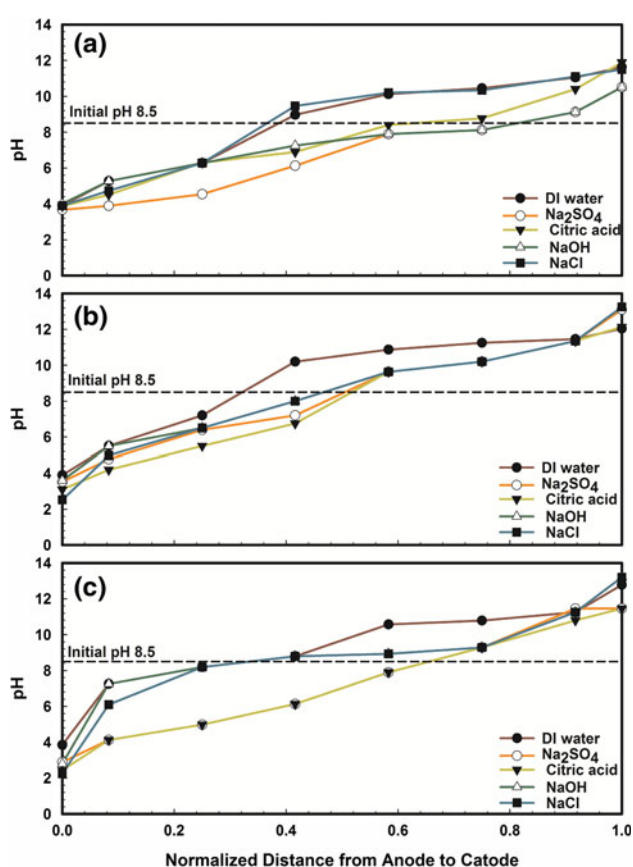
The energy expenditure in the investigated systems was calculated as follows:

$$E_u = \frac{P}{V_s} = \frac{1}{V_s} \int V I dt \quad (10)$$

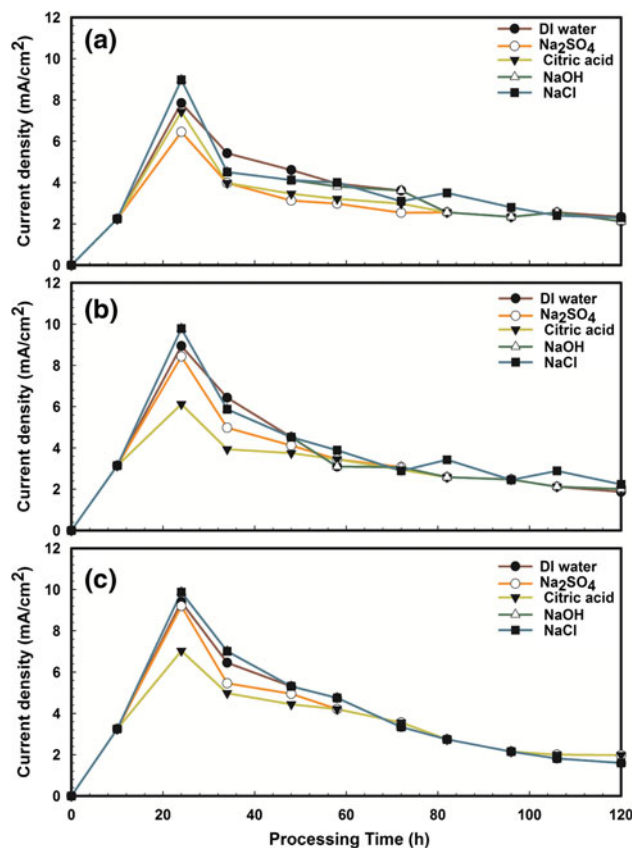




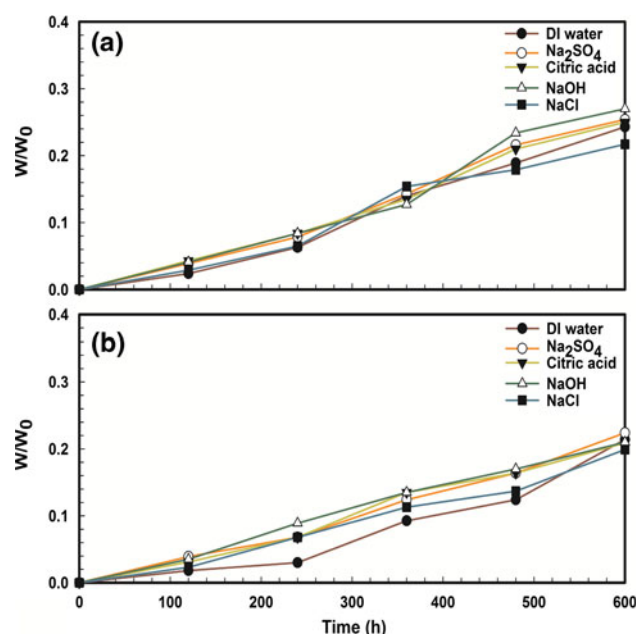
**Fig. 5** Progressive cyclic voltammogram for RT electrode in solution of **a** 0.1 M citric acid; **b** 0.1 M  $\text{Na}_2\text{SO}_4$ ; **c** 0.1 M NaOH; **d** 0.1 M NaCl (without BPA)



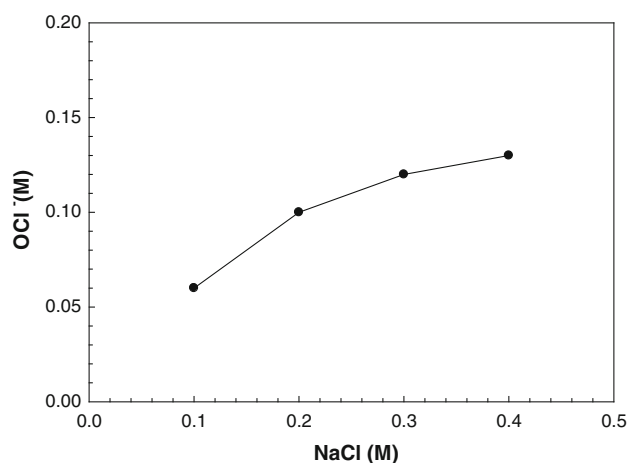
**Fig. 6** The pH profile in systems of **a** EK-Ti; **b** BMOEEK-PT; and **c** BMOEEK-RT (Duration: 5 days; Potential gradient:  $2 \text{ Vcm}^{-1}$ )



**Fig. 7** The current density as a function of time in systems of **a** EK-Ti; **b** BMOEEK-PT; and **c** BMOEEK-RT. (Duration: 5 days; Potential gradient:  $2 \text{ Vcm}^{-1}$ )



**Fig. 8** Detachment of coated metals in BMOEEK systems versus time. **a** Pd/Ti electrode; **b** RT electrode



**Fig. 9** The production of  $\text{OCl}^-$  versus concentration of NaCl in investigated system

where  $E_u$  is the energy expenditure per unit volume of soil ( $\text{kWh m}^{-3}$ );  $P$  is the energy expenditure ( $\text{kWh}$ );  $V_s$  is the volume of soil ( $\text{m}^3$ );  $V$  is the volume of the electrolyte ( $\text{m}^3$ );  $V$  is the voltage (V);  $I$  is the current (A); and  $t$  is the time (h). In the constant voltage tests, the energy expenditure is directly related to the time integral of the current across the cell. The calculated energy consumption was 541.2–748.5, 508.2–643.1, and 542.4–721.5  $\text{kWh m}^{-3}$  for the EK–Ti, BMOEEK–PT, and BMOEEK–RT systems, respectively (column 5 in Table 1). The results showed that the processing fluid and binary metallic oxidation electrodes were important determinants of the energy consumption of investigated systems.

### 3.4 BPA remediation mechanisms in BMOEEK systems

Two mechanisms, namely, migration to the reservoirs by electroosmotic flow [33] and degradation by anode oxidation in the reservoirs [34, 35] were dominant for the remediation of BPA in the investigated systems. The  $\text{pK}_a$  of BPA is 9.6, which means that BPA will dissociate in its anionic form when the pH is greater than 9.6 and in its neutral form when the pH is less than 9.6. Therefore, BPA could migrate either toward the anode reservoir by electromigration or toward the cathode reservoir by electroosmotic flow. The BPA removed in the anode reservoir would be degraded by the binary metallic oxidation electrode.

To clarify the remediation mechanisms of BPA in the investigated systems, the BPA retained in the reservoirs and soil were quantified for each test. Four important parameters, namely, the removal efficiency ( $R$ ), degradation efficiency ( $\eta$ ), residual ( $S$ ), and treatment efficiency ( $Y$ ) of BPA, were defined as Eqs. (11)–(14).

$$R = \frac{W_0 - W_{\text{soil}}}{W_0} \times 100 \% \quad (11)$$

$$\eta = \frac{W_0 - W_{\text{soil}} - W_{\text{reservoir}}}{W_0} \times 100 \% \quad (12)$$

$$S = \frac{W_{\text{soil}}}{W_0} \times 100 \% \quad (13)$$

$$Y = R + \eta \quad (14)$$

where  $W_0$  is the initial BPA (mg),  $W_{\text{soil}}$  is the BPA retained in soil (mg),  $W_{\text{reservoir}}$  is the BPA collected in reservoirs (mg)

As shown in Table 1, the fraction of BPA in the anode reservoir (column 6) was much lower than that in the cathode reservoir (column 8) in all systems, which was in agreement with Yuan et al. [16]. The degradation of BPA by anodic oxidation resulted in less BPA collected in the anode reservoir. Owing to the sum of BPA collected and degraded in anode reservoir (columns 6 and 7 in Table 1) was greater than the BPA collected in the cathode reservoir, more BPA migrated to the anode by electromigration mechanism than migrated to the cathode by electroosmosis flow.

The results of fractional distribution of BPA in degradation, removal, and residual phases in the EK and BMOEEK systems in Table 1 were plotted in Fig. 10. The fraction of residual BPA in investigated systems was ranked as follows in terms of the processing fluid:  $\text{DW} > \text{Na}_2\text{SO}_4 > \text{CA} > \text{NaOH} > \text{NaCl}$ . This trend was mainly attributed to the higher solubility of BPA in the other four solutions than in DW. Similarly, the fraction of BPA removal in the BMOEEK systems was ranked as follows in terms of processing fluid:  $\text{DW} > \text{Na}_2\text{SO}_4 > \text{CA} > \text{NaOH} > \text{NaCl}$  (Fig. 10b, c). It was found that the BPA removal was dramatically lower in the NaCl systems,

which might be due to the removed BPA being degraded by the binary metallic oxidation electrodes.

As more BPA was pushed out from the soil to the anode reservoir, the mechanism of anode oxidation became dominant. The results showed that the best degradation ability was found in the NaCl system (Fig. 10), following the order BMOEEK–RT (61.0 %) > BMOEEK–PT (51.5 %) > EK–DW (30.2 %). The degradation performance was strongly related to the electrode type and the coating efficacy of the electrodes. As shown in Sect. 3.1, less  $\text{Ru}^{2+}$  was coated on the electrodes ( $1.42 \pm 0.15$  %) than  $\text{Pd}^{2+}$  ( $1.60 \pm 0.09$  %). This finding clearly indicated that the oxidation ability of BPA was better with the RT electrode than the PT electrode.

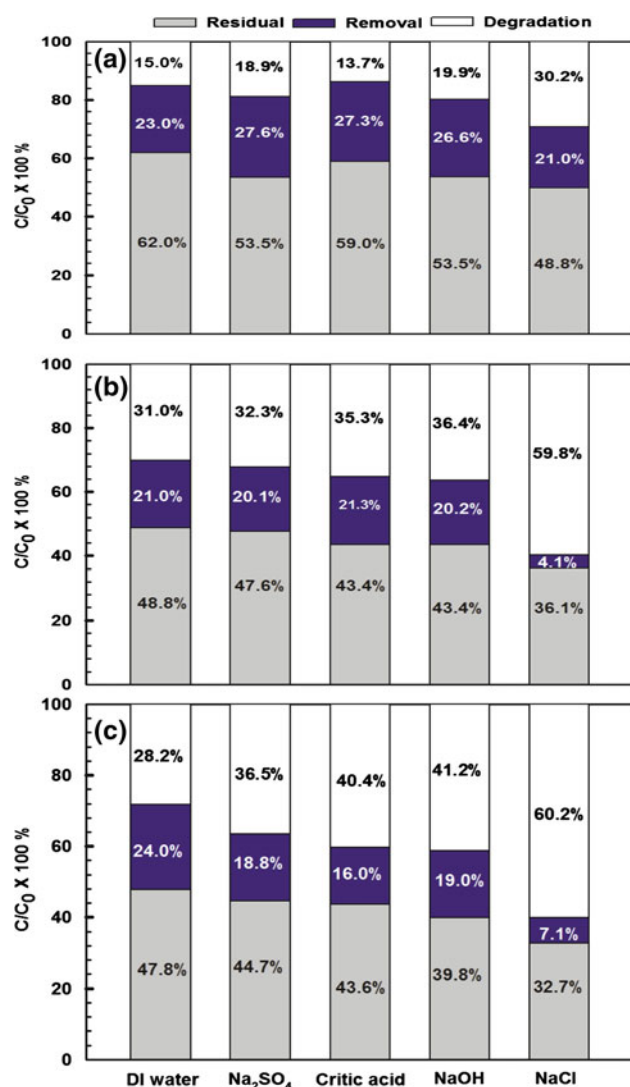
In summary, the degradation mechanism was more critical for BPA remediation than the EK removal

mechanism was. Furthermore, among the EK removal mechanisms, electromigration was dominant for the migration of BPA. The results in Fig. 8 concluded that the remediation performance of BPA was strongly related to the oxidation ability of electrodes and electrolyte solutions.

#### 4 Conclusions

The RT electrodes have been reported successfully degraded organic contaminants, and the palladium is a potential metal for preparation reactive electrodes. Hence, the RT and Pd/Ti electrodes were applied in electrokinetic system to investigate the BPA degradation performance. Two important contributions were reached in this study: (1) the electrokinetic process was confirmed to be a successful technology for the remediation of environmental hormone-contaminated soil; and (2) the application of binary metallic oxidation electrodes of RT and Pd/Ti electrodes in EK processes has been upgraded to a sustainable technology because the treatment mechanisms include not only removal but also degradation of BPA. The primary conclusions of this study may be summarized as follows:

- (1) A typical irreversible electrode reaction was found in the investigated binary metallic oxidation electrodes in cyclic voltammograms. The corresponding potentials of the peak current in the BMOEEK–PT system was lower than that in the BMOEEK–RT system, which implied that the RT electrode required a higher voltage to initiate oxidation. Furthermore, the oxidation behavior of the binary metallic oxidation electrodes was strongly related to the electrolyte solutions.
- (2) The remediation performance of BPA in the BMOEEK systems was highly dependent on the electrode and processing fluid. The best treatment efficiency (67.3 %) was found for the BMOEEK–RT system with NaCl as the processing fluid. This high performance is attributed to the concentrations of both  $\text{OCl}^-$ , and the OH radical contributed to BPA degradation in NaCl solution.
- (3) The best degradation ability was found in the NaCl system, in the order of BMOEEK–RT (61.0 %) > BMOEEK–PT (51.5 %) > EK–DW (30.2 %). Less  $\text{Ru}^{2+}$  coated on the electrode, however, resulted in increased BPA degradation, which might be due to the relative oxidation abilities of the electrodes for BPA degradation being RT Pd/Ti.
- (4) The RT electrode showed a longer life cycle and a higher oxidation ability of BPA than Pd/Ti electrode.
- (5) In the investigated systems, the degradation mechanism was more critical for BPA remediation than EK removal mechanism was. Furthermore, among the EK



**Fig. 10** Fractional distribution of BPA in systems of **a** EK–Ti; **b** BMOEEK–PT; and **c** BMOEEK–RT. (Duration: 5 days; Potential gradient:  $2 \text{ V cm}^{-1}$ )

removal mechanisms, electromigration was dominant for the migration of BPA. It was concluded that the remediation performance of BPA was strongly related to the oxidation ability of the electrodes and electrolyte solutions.

- (6) The mineralization performance and degraded products of BPA by binary metallic oxidation electrodes requires further investigation.

**Acknowledgments** This research was funded by the National Science Council of Taiwan, Grant # NSC 99-2211-E-390-008-MY3. The authors are grateful to the reviewers for their valuable comments.

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